ENVIRONMENTAL MONITORING OF THE 1987 GYPSY MOTH ERADICATION PROJECT IN LOS ANGELES COUNTY

JANUARY 1989

Environmental Hazards Assessment Program

STATE OF CALIFORNIA
Department of Food and Agriculture
Division of Pest Management, Environmental Protection and Worker Safety
Environmental Monitoring and Pest Management Branch
1220 N Street, Sacramento, California 95814

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ENVIRONMENTAL MONITORING OF THE 1987 GYPSY MOTH
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REPORT - NO. 89-1

E R R A T A

Page 11, lines 9-10 should read:

"At property 1, residues appeared to initially increase over time and then had a tendency to degrade ($.05 < P \leq .10$)."

Page 12, footnote 3 should read:

* denotes marginal significance ($0.05 < P \leq 0.10$).

State of California

Memorandum

To : John Sanders, Ag. Program Supervisor
Environmental Hazards Assessment Program

Date : January 6, 1989

Place : Sacramento

Phone: 3-3682

From : **Department of Food and Agriculture** Joey Marade, Environ. Hazards Scientist
Environmental Hazards Assessment Program

Subject: Executive Summary for the Report "Environmental Monitoring of the 1987 Gypsy Moth Eradication Project in Los Angeles County"

In the spring of 1987, the California Department of Food and Agriculture (CDFA) initiated a program to eradicate an infestation of the gypsy moth in the Encino area of Los Angeles County. One phase of the eradication program consisted of two applications of diflubenzuron (Dimilin) to all foliage on nine properties surrounding the detection site.

The Environmental Hazards Assessment Program of the CDFA monitored diflubenzuron concentrations on foliage and in soil, air, and water for eight weeks during the treatment program. Diflubenzuron residues in all sampling media were low after both applications but relatively higher following the second application. Increases were due to remaining residues from the first application and a greater volume of pesticide applied during the second application. Additional foliage and soil samples taken over a longer time period would be needed to establish a more defined dissipation trend.

SURNAME SO-106	Marade	Weaver				

Environmental Monitoring of the 1987 Gypsy Moth Eradication Project in Los Angeles County

by

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ABSTRACT

The Environmental Hazards Assessment Program monitored two properties for an eight week period to document the environmental levels of diflubenzuron on foliage, and in soil, water and air samples during the 1987 Los Angeles County Gypsy Moth Eradication Project. Diflubenzuron residues detected in all sampling media were low after both applications but relatively higher after the second application. Greater foliar residue detected after the second application was most likely due to a combination of a greater volume of pesticide applied during the second application and residual pesticide remaining on foliage from the first application. A curvilinear degradation trend was measured on foliage after the second application. However, a greater number of samples over a longer period of time would be required to validate this pattern. Soil residues degraded at an average rate of 0.01 ppm per day at both sites following the second spray.

ACKNOWLEDGMENTS

A very special thank you to Bonnie Turner, Jacob Aniku, John Sitts, and Kim Worl for their contributions to this project along with Vince Bunac, Jesse Ybarra, Gilbert Bejarano, and Debbie Fernandez for their assistance in preparing materials and supplies during the program.

Also, to the people of the Gypsy Moth Eradication Project for their cooperation in the coordination of this study. A special thanks to Juan Mercogliano and his crew at the field sites.

Thank you Donald Weaver for your comments and suggestions with this report.

Much appreciation to Sally Powell for the computer generated graphics and to Linda Heath for preparing the map of the treatment area.

And finally, a much deserved thank you to two very cooperative families who allowed us to monitor their properties during this project.

DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such product.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The State of California has placed a high priority on protecting the State from any infestation by Lymantria dispar, commonly known as the gypsy moth, because of potential economic impacts on California agriculture. Past outbreaks in the Eastern United States have resulted in the defoliation of trees and shrubs (1). Trapping data from two consecutive years (1985-86) in the Encino area of Los Angeles County indicated that the Gypsy moth was becoming established in that area. Consequently, the Director of the California Department of Food and Agriculture (CDFA) authorized the Division of Plant Industry (PI) to proceed with an eradication effort. A report describing the impact and history of the gypsy moth as well as the alternatives that were available to PI to eradicate this pest was prepared by Loughner et. al. (1).

The eradication effort included four aerial applications of Bacillus thuringiensis (BT) over a 40 acre treatment area and two ground treatments of diflubenzuron (Dimilin®) at 9 properties in the center of the BT treatment area surrounding the positive trap sites. In addition, the Environmental Hazards Assessment Program (EHAP) was requested to implement a monitoring program to document the environmental levels of diflubenzuron on foliage and in soil, water and air during the treatment program. This report contains the levels of diflubenzuron residue detected during an eight week monitoring period.

MATERIALS AND METHODS

Treatment Area

Nine properties surrounding the two 1986 positive trap sites were treated with diflubenzuron. These nine properties were in the center of a larger 40 acre zone that received four aerial applications of *Bacillus thuringiensis* in the Encino community of Los Angeles County (Figure 1).

The terrain consisted of both flatland and moderately steep hillsides. Houses were terraced on the hillsides. Landscapes blended ornamental plantings with natural vegetation. This vegetation included *Eucalyptus spp.*, sycamore, pine, liquidambar, and a combination of deciduous and evergreen fruit trees. Vegetation was described as mature with the trees ranging from 20 to 100 feet in height (2). No natural waterways were located in the area.

Treatment Method

Diflubenzuron (Dimilin® WP-25) was applied twice in the spring of 1987 with a 3 week interval between sprays. Applications were made by hydraulic ground spray rigs (Gun-Jet® orchard spray gun, orifice D-8, 200 psi) to all foliage on the nine properties. Diflubenzuron was applied with rate of 0.5 ounces active ingredient (AI) per 100 gallons of water (0.0039% AI) to the point of drip on the foliage. The application crew tarped swimming pools, fish ponds, bird baths, and any other sensitive areas prior to treatment to prevent exposure to the spray.

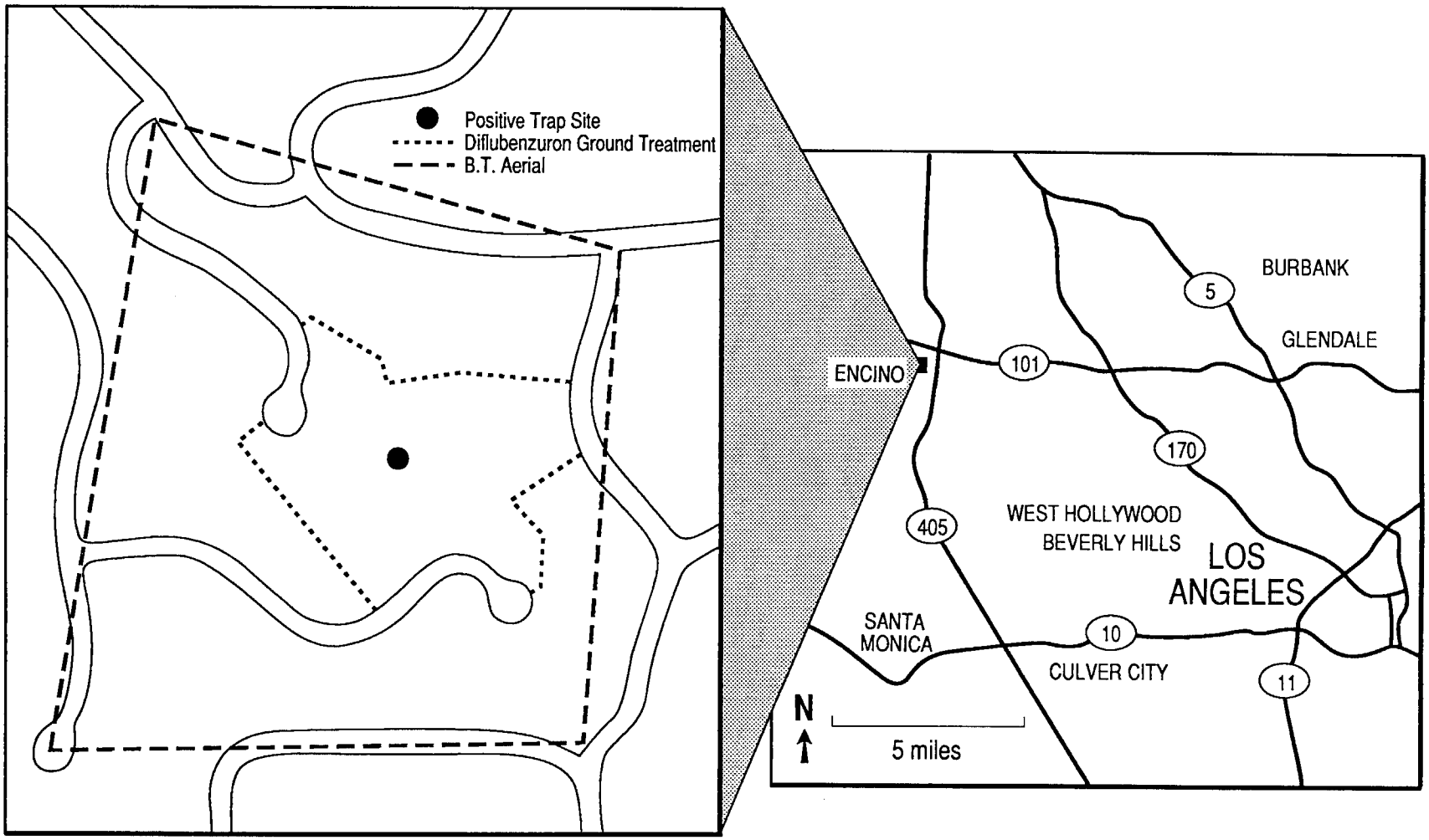

Figure 1. Ground treatment and aerial treatment zones in Encino, CA for the Los Angeles Gypsy Moth Eradication Project, 1987.

Study Design

The dissipation of diflubenzuron was monitored in two properties that were representative of the general characteristics of the study area, provided ample amounts of each of the desired sampling media, and belonged to property owners who were agreeable to repeated access to their property during an eight-week sampling program. Five to six different trees or bushes with varying heights and fullness were selected on each property. Soil samples were obtained beneath the canopy of the trees selected for foliar sampling. The terrain consisted of both flat areas and moderately inclined hillsides. Since no natural waterways were located in the study area, water samples were taken from Koi fish ponds at both properties. Residential air sample sites were located outside near the patio or front doors at each property at a point where one could have observed the pesticide application.

Sample Schedule and Collection

Background foliage, soil, and water samples were collected one day prior to the start of the treatment program. The background air sampling schedule and post application schedule for all media were as follows:

Foliage - once per week for eight weeks

Soil - once per week for eight weeks

Air - background: evening before application (between 6 and 9 pm)
- at onset of application until 10 minutes after application
- immediately after application (3 hour duration)
- 24 hour post application (3 hour duration)

Water - collected 30 minutes after each application.

Tank - one sample from each load of tank mix prepared on site.

Sampling Methods

Standard EHAP sampling techniques and data collection procedures were followed (3, Appendix I) for collecting foliage, soil, air, and surface water samples. A brief description of each method follows:

Foliage - At each property, two replicate leaf samples were collected for analysis of dislodgeable residue. Each sample was comprised of approximately 40 leaves collected at random from each quadrant of five (property 2) or six (property 1) treated trees. The same trees were used throughout the foliar study.

Soil - At each property, two replicate surface soil samples were collected from the top 2.5 centimeters. Each sample was comprised of approximately 500 grams of soil collected at random from each quadrant beneath the five or six treated trees selected for foliage sampling. The sample included any thatch gathered by the sampler.

Air - Two non-replicated air samples per collection period were collected at each property using high volume air samplers. Originally, replicate XAD-2 resin jars were planned to be placed on the high volume air samplers for use as the collection media. However, the laboratory encountered difficulty in producing a useful diflubenzuron extraction method for the resin samples. Instead, a glass fiber filter (GFF) was used as a precautionary measure if a method could not be developed for the resin jars. An XAD-2 resin jar was

placed on the first sampler while a GFF was placed on the second sampler to capture diflubenzuron in the air. The non-replicated samplers were calibrated to draw 1000 liters of air per minute through each sampling medium. All background and post-application sampling periods were three hours in duration; the application sampling period coincided with the time of application to the property.

Water - Two replicate surface water samples were collected at each site. A Nalgene® hand-operated pump with Teflon® tubing was used to collect the surface water samples from each koi pond. The bottles were completely filled, sealed with aluminum foil, capped, and immediately placed on wet ice.

Tank - One tank sample was obtained from each load of tank solution applied to the property. The spray tank mixture was agitated for a minimum of 5 minutes prior to collection of 1 pint of spray in a wide-mouth quart jar. Samples were capped, sealed in two plastic bags, and stored on wet ice in a separate cooler from the rest of the samples.

Laboratory Methods

The California Department of Food and Agriculture, Chemistry Laboratory Services Branch (CDFA Lab) in Sacramento, CA performed the chemical analyses of all samples for this monitoring program. Samples were analyzed for diflubenzuron using high pressure liquid chromatography (HPLC) (Appendix II).

Quality Control Methods

Continual intralaboratory quality control procedures were in effect during the study. Blank-matrix spikes were prepared by adding known amounts of diflubenzuron to pesticide-free samples for each media. One blank-matrix spike sample was analyzed with each extraction set to determine the accuracy of the analysis.

A trapping efficiency study was performed to evaluate the collection of diflubenzuron on XAD-2 resin and GFF. Five replicate XAD-2 resin sampling jars and five GFF air sampling media were each analyzed at two levels of fortification (1 ug and 1,000 ug). Each of the five replicate samples (XAD-2 resin jar or GFF) were mounted on separate hi-volume air samplers and spiked with the appropriate amount of diflubenzuron during the fortification trial. The air sampler ran for three hours at a flow rate of 1,000 liters per minute. The XAD-2 resin or GFF were sealed in plastic bags and aluminum foil, respectively, then immediately delivered to the CDFA Lab for recovery analysis.

Laboratory Reports

CDFA Lab reported the sample analyses results to EHAP as follows:

Foliage : Total micrograms dislodged from sample. Minimum detectable level (MDL) was 0.5 ug.

Soil : Parts per million (ppm) found in a 100 gram dry weight sample with an MDL of 0.02 ppm.

Air : Total amount of diflubenzuron captured on GFF during the sampling period. MDL was 0.4 ug.

Water : Parts per billion (ppb) in the sample with a MDL of 0.5 ppb.

Tank : Percentage of active ingredient diflubenzuron found in each tank sample.

Statistical Methods

The concentrations of diflubenzuron found in soil, water, and tank media were reported by CDFA Lab chemists. Foliar concentrations of diflubenzuron were corrected for leaf area and weight and are reported in micrograms per square centimeter (surface area basis) and parts per million (dry weight basis), respectively. Air results are presented as micrograms of diflubenzuron detected per cubic meter of air that passed through the equipment. Air samplers were calibrated to pass 1 cubic meter (1000 liters) of air per minute.

Within each spray, degradation trends for diflubenzuron in foliage and soil were explored using linear regression techniques with days since application as the independent variable in both simple linear regression and second-order polynomial models.

RESULTS

Foliage

Results from the chemical analysis of foliar samples for diflubenzuron residues are presented in Tables 1 and 2. None of the background samples yielded measurable amounts of diflubenzuron.

Table 1. Concentrations of diflubenzuron residues (ppm) detected on replicate foliage samples collected from two properties during the 1987 Los Angeles County Gypsy Moth Eradication Program.

Days Post Application	Foliar Residue[a] (ppm, dry weight) Property 1 Replicate 1	Property 1 Replicate 2	Property 2 Replicate 1	Property 2 Replicate 2	Mean All Reps
Application 1					
0	5.186	2.276	---[b]	---	3.731
1	---	---	3.457	2.367	2.912
6	LS[c]	LS	LS	LS	LS
13	1.757	1.595	2.941	4.499	2.698
Application 2					
1	6.531	5.693	11.522	7.591	7.834
7	7.191	9.593	9.235	9.869	8.972
14	11.076	10.999	6.595	8.167	9.209
21	15.409	13.647	12.621	19.136	15.203
28	12.725	11.676	10.567	12.790	11.940

a. No diflubenzuron residue was detected on background samples.

Concentrations were calculated on a dry weight basis.

b. --- represents no sample for that particular post application period.

c. LS represents lost sample.

Table 2. Concentration of diflubenzuron residues (ug/cm2) detected on replicate foliage samples collected from two properties during the 1987 Los Angeles County Gypsy Moth Eradication Program.

	Foliar Residue[a] (ug/cm^2)				
	Property 1		Property 2		Mean
Days Post Application	Replicate 1	Replicate 2	Replicate 1	Replicate 2	All Reps
Application 1					
0	0.082	0.035	---[b]	---	0.059
1	---	---	0.031	0.021	0.026
6	LS[c]	LS	LS	LS	LS
13	0.024	0.021	0.028	0.044	0.029
Application 2					
1	0.093	0.081	0.114	0.072	0.090
7	0.098	0.128	0.088	0.097	0.103
14	0.154	0.167	0.070	0.086	0.119
21	0.218	0.205	0.123	0.191	0.184
28	0.186	0.169	0.114	0.145	0.154

a. No diflubenzuron residue was detected on background samples.

b. --- represents no sample for that particular post application period.

c. LS represents lost sample.

Following the first spray, dislodgeable foliar levels of diflubenzuron ranged from 0.021 to 0.082 ug/cm^2. The analysis of the foliar samples collected on days 0, 1, and 13 did not yield a clear degradation trend. Although samples were collected on day 6 as outlined in the protocol, samples were lost enroute to the laboratory. Mean dislodgeable foliar residues were 0.029 ug/cm^2 13 days after the initial spray.

A higher degree of within property variability and generally higher residue levels were observed for foliar samples collected following the second spray (Figure 2). At property 1, residues appeared to initially increase over time and then had a tendency to degrade ($.10 \leq P < .05$). This degradation trend was not evident until nearly 30 days after the second spray (Table 3). Similar trends were noted at property 2; however, regression models fitted to these data were not significant ($P > 0.50$, Table 3). This apparent increase may have resulted from high levels of variability. A greater number of replicates collected over a longer sampling period would be required to more accurately detect the true underlying degradation pattern for diflubenzuron on foliage.

Soil

Results of the chemical analyses of diflubenzuron in soil are presented in Table 4 and Figure 3. As may be observed from Table 4, diflubenzuron soil residues following the second spray were substantially higher at both properties with measured residues for property 2 following the second spray

Table 3. Summary of regression models[1] of diflubenzuron residues detected on foliar and soil samples from two properties following the second spray of the 1987 Los Angeles County Gypsy Moth Eradication Program.

		Residue		
Property	Parameter	Foliar (ug/cm^2)	Foliar (ppm)	Soil (ppm)
1	Intercept	0.068	4.945*	0.19
	Linear Term	0.010	0.690	-0.003*
	Quadratic Term	-0.002	-0.014	---[2]
	R-squared	0.90	0.91	0.45
	Model Significance	0.10*	0.09*	0.21
2	Intercept	0.087	8.883*	0.45**
	Linear Term	0.0006	0.082	-0.012*
	Quadratic Term	-0.00005	0.003	---[2]
	R-squared	0.48	0.28	0.59
	Model Significance	0.52	0.72	0.13

1. Soil data were modeled by a simple linear model $Y = B_0 + B_1X$. Foliar data were modeled by a polynomial regression model of the form $Y = B_0 + B_1X + B_2X^2$.
2. Quadratic term was not included in analyses of soil data.
3. * denotes marginal significance ($0.05 < P \leq 0.010$).
4. ** denotes statistical significance ($P \leq 0.05$).

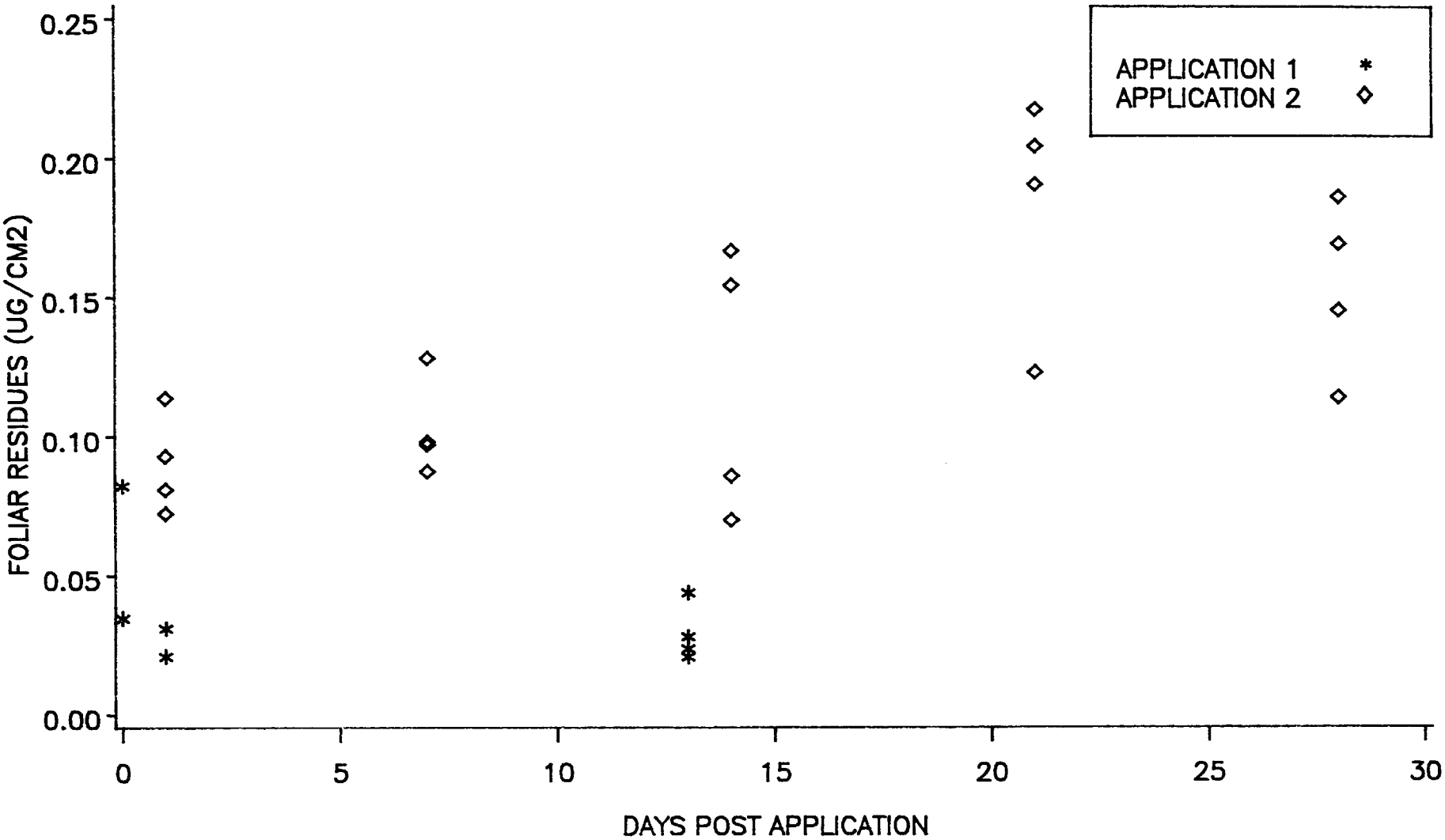

FIGURE 2: DIFLUBENZURON FOLIAR RESIDUES (UG/CM2).
DATA SHOWN FOR TWO PROPERTIES IN LOS ANGELES COUNTY.

Table 4. Concentrations of diflubenzuron residues detected in soil samples collected from two sites during the 1987 Los Angeles County Gypsy Moth Eradication Program.

	Soil Residue[a] (ppm, dry weight)				
	Property 1		Property 2		Mean
Days Post Application	Replicate 1	Replicate 2	Replicate 1	Replicate 2	All Reps
Application 1					
0	0.10	0.06	--[b]	--	0.08
1	--	--	0.07	ND[c]	0.04
6	0.09	0.09	0.08	0.06	0.08
13	0.17	0.06	0.04	0.09	0.09
Application 2					
1	0.16	0.20	0.70	0.46	0.38
7	0.17	0.24	0.25	0.24	0.23
14	0.08	0.13	0.27	0.10	0.15
21	0.19	0.13	0.07	0.27	0.17
28	0.13	0.09	0.27	0.10	0.15

a. Detection limit was 0.02 ppm.

b. --- represents no sample for that particular post application period.

c. ND represents none detected.

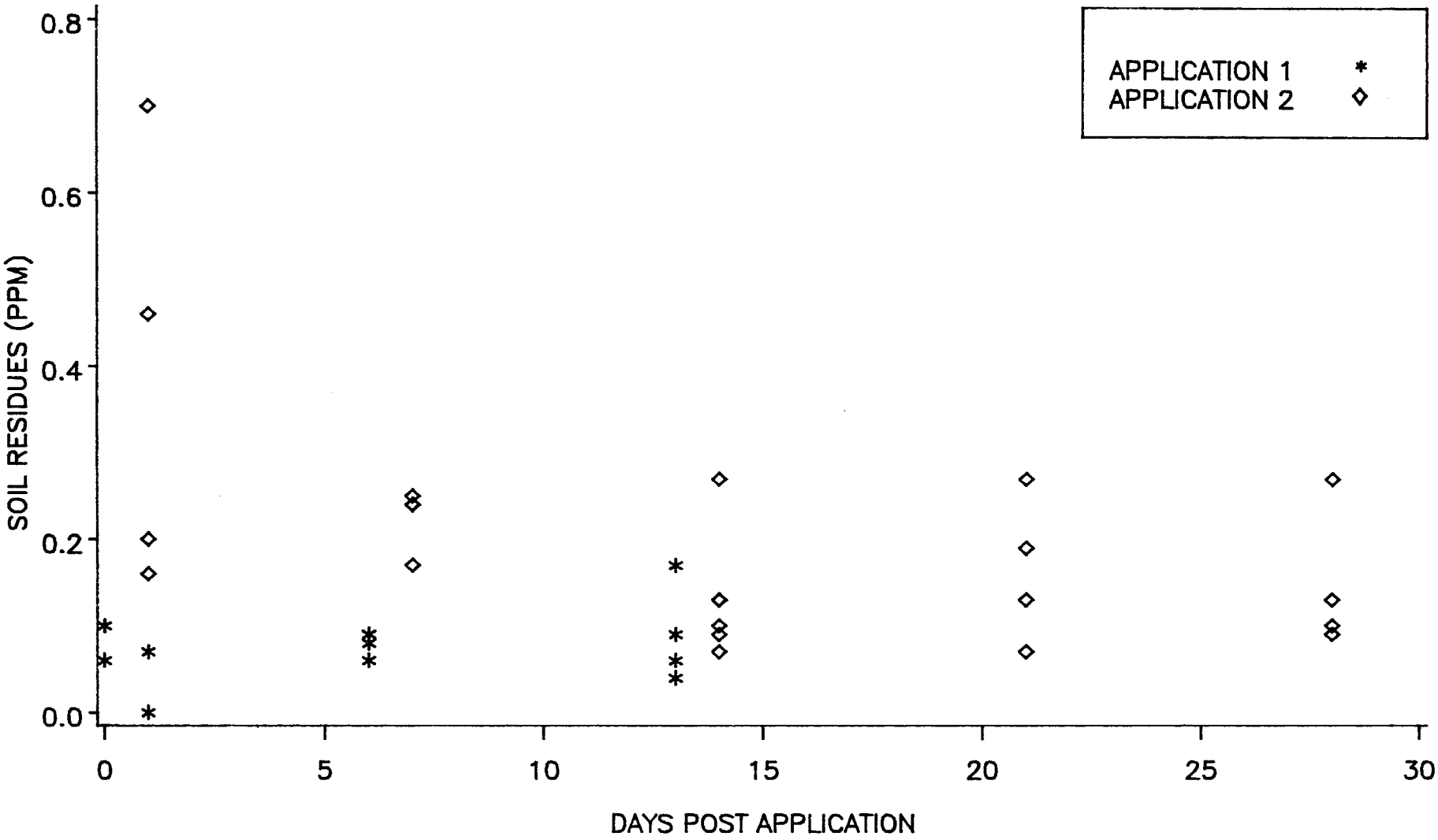

FIGURE 3: DIFLUBENZURON SOIL RESIDUES (PPM).
DATA SHOWN FOR TWO PROPERTIES IN LOS ANGELES COUNTY.

over twice those measured for property 1. Average soil residues were 0.58 ppm at property 2 compared with 0.18 ppm at property 1. Prior to the first spray, diflubenzuron residues of 0.1 ppm were detected in one composited soil sample at property 2. The presence of detectable diflubenzuron residues in this background sample indicates possible off-target drift from previously treated adjacent properties.

All but one post-treatment soil sample contained measurable amounts of diflubenzuron ranging from 0.04 to 0.70 ppm (Table 4). Soil residues had a tendency to degrade at an average rate of approximately 0.01 ppm per day at both properties following the second spray (Table 3). At 28 days after the second spray, average soil residues were 0.11 ppm at property 1 and 0.19 ppm at property 2.

Air

Due to difficulty encountered in producing a useful extraction method for the resin samples only the GFF samples were analyzed for diflubenzuron. The highest concentration found was 0.769 ug/m^3 at property one during the second application. The differences in air concentration between the two sites may be attributed to the closer proximity of the air sampler to treated foliage at property 1 than at property 2. No diflubenzuron was detected in post treatment samples following the first application. There was an increase of diflubenzuron air concentrations for both sites during the second application (Table 5) which may be attributed to the increase in the number of tank loads of pesticide applied to the properties (Table 6).

Table 5. Concentration of diflubenzuron detected in air samples collected for the 1987 Los Angeles County Gypsy Moth Eradication Project.

Application	Sampling Period and Concentration[a] (ug/m^3)			
	Background	During	Immediate Post	24 Hour Post
Property 1				
1	N.D.[b]	0.076	N.D.	N.D.
2	N.D.	0.769	0.008	0.008
Mean	0.000	0.423	0.004	0.004
S.D.	0.000	0.490	0.006	0.006

Application	Sampling Period and Concentration[a] (ug/m^3)			
	Background	During	Immediate Post	24 Hour Post
Property 2				
1	N.D.[b]	0.024	N.D.	N.D.
2	N.D.	0.193	0.005	0.004
Mean	0.000	0.109	0.003	0.002
S.D.	0.000	0.120	0.004	0.003

a. Detection limit was 0.002 ug/m^3.

b. N.D. represented None Detected.

Table 6. Concentrations of diflubenzuron in tank samples taken during the 1987 Los Angeles County Gypsy Moth Eradication Project.

	Diflubenzuron (%)[a]	Amount Relative to theoretical concentration (%)
Property 1		
Application 1		
Tank #1	0.0046	118
#2	0.0044	113
Application 2		
Tank #1	0.0046	118
#2	0.0046	118
#3	0.0044	113
#4	0.0041	105
Property 2		
Application 1		
Tank #1	0.0081	208
#2	0.0038	97
Application 2		
Tank #1	0.0041	105
#2	0.0045	115
#3	0.0046	118

a. Desired theoretical percentage of diflubenzuron in 100 gallon tank of water was 0.0039%. Tank samples were obtained from a 100 gallon tank solution containing 0.5 ounces active ingredient diflubenzuron.

Small quantities of pesticide were detected in post-treatment samples at both properties following the second spray.

Tank

Ten of the eleven tank samples analyzed contained between 97% and 118% of the desired amount of 0.0039% active ingredient of diflubenzuron. One sample had 0.0081% AI diflubenzuron detected which is equivalent to 208% of the desired amount in the formulation (Table 6).

Water

No diflubenzuron was recovered from surface water samples collected after each application at either site.

Quality Control

Six spiked water samples were submitted for analysis and resulted in recoveries ranging from 80 to 100 percent (Table 7). One sample was lost during analysis. Glass fiber filter quality control analyses included one blank GFF and two spiked GFFs fortified with 5 ug of diflubenzuron. No diflubenzuron was detected on the blank sample while 96 and 98 percent of the diflubenzuron was recovered from the spiked GFFs. Foliar QC work consisted of two surten-water spikes, one spiked at the 5 ug level and the other at the 15 ug level, and a reagent spike of 3 ug diflubenzuron. Recovery rates for the three spikes were 92, 96, and 99 percent, respectively. No diflubenzuron was detected in four soil blank matrix samples and diflubenzuron recovered from spiked soil samples ranged from only 30 to 60 percent (Table 8).

Table 7. Recovery of diflubenzuron from water samples spiked at various levels and submitted to CDFA Lab for quality control analysis.

Spike level ppb	Amount Recovered	Percent Recovery
1	0.8	80
1	0.8	80
4	3.3	82
5	5.0	100
8	6.6	82

Table 8. Residue recovery results for soil samples spiked with 0.1 ppm diflubenzuron as a quality control procedure.

Spike	Diflubenzuron ug/g (ppm found)	Diflubenzuron Percent Recovered
1	0.06	60
2	0.03	30
3	0.03	30
4	0.03	30

Number of observations = 4

Mean Recovery = 37.5

Standard deviation = 15.0

The GFF portion of the trapping effiency study yielded recovery rates averaging 82 and 91.8 % for the 100 ug and 1,000 ug tests, respectively (Table 9). None of the XAD-2 resin jars were analyzed due to the difficulty encountered in producing an extraction method.

Table 9. Results of the Gypsy Moth diflubenzuron trapping efficiency study performed April 16, 1987 at spike levels of 100 ug and 1000 ug diflubenzuron per 1 ml volume solution.

	Glass Fiber Filter	
	Test Number 1	Test Number 2
	Percent Recovery	Percent Recovery
Sample Number	100 ug / 1 ml	1000 ug / 1 ml
1	82	84
2	82	84
3	82	94
4	82	103
5	82	94
Number of Observations	5	5
Mean Recovery	82	91.8
Standard Deviation	0.0	8.0

DISCUSSION

The residue levels of diflubenzuron detected on foliage and in soil samples were low with respect to levels that could have been acutely toxic to mammals, birds, fish and bees (4). Both the foliar and soil data indicated that residues persisted during the 8-week sampling program but a greater number of samples over a longer period of time would have been necessary to define the dissipation trend.

Other studies summarized by Dobroski et al. determined that diflubenzuron on foliage surfaces was persistent, exhibited rainfastness, and that residue levels decreased because of dilution by growth (5). Dobroski cited a study by Bull and Ivie (6) who noted that over 50% of the diflubenzuron applied to cotton leaves in an indoor environment was still detected 28 days after application. Characteristics that may have accounted for the persistent residues include a high attraction of diflubenzuron to the leaf surface, slow sorption into leaves, and low volatility.

Furthermore, diflubenzuron was not mobile in soil and the soil half-life was related to microbial activity and particle size (5). The half-life of a 10 um particle was 16 weeks compared to one week for a 2 um particle (7). The smallest droplet size obtained from the spray equipment under standard operator practices used in the eradication program was 350 to 400 um (8). Thus, the size of the diflubenzuron particle may, in part, explain the persistence that was measured over the eight-week period. Soil residues had a tendency to degrade at an average rate of approximately 0.01 ppm per day

at both properties following the second spray which may have been related to microbial degradation.

Air sampling results also showed that low concentrations of diflubenzuron were in the air during both applications and up to 24 hours after the second application was completed. However, the highest concentration detected, 0.769 ug/m^3, occurred at property 1 during the second application. Higher levels of diflubenzuron found in foliage, soil and air samples after the second application were most likely due to a combination of a greater volume of pesticide applied during the second application and residual pesticide remaining on foliage and soil media from the first application. No residues were detected in any of the water samples. The exposure of aquatic species to diflubenzuron was minimized because of the lack of natural waterways located in the study area and the efforts of the eradication crew to prevent drift into manmade fish ponds by tarping these areas.

The results of previous EHAP monitoring studies of gypsy moth eradication projects (9,10) indicated that carbaryl residue levels detected on foliage samples immediately after hydraulic ground spray application were over 30 times greater than diflubenzuron levels observed on foliage samples during this monitoring program. This can be attributed to a lower concentration of diflubenzuron in the tank mix, 0.0039% active ingredient, compared to 0.120% carbaryl active ingredient.

LITERATURE CITED

(1) Loughner, George E., et al. January 1987. Environmental Assessment of Gypsy Moth and Its Eradication in California, 1987 Program. California Department of Food and Agriculture. Sacramento, CA. 76 pp.

(2) Zadig, Dorthea. November 1986. Addendum to Environmental Statement of Gypsy Moth and Its Eradication in California, 1987 Program. Gypsy Moth Site Summary and Proposed Treatment Plan, Los Angeles County, 1987. California Department of Food and Agriculture. Sacramento, CA. 4 pp.

(3) Sava, R.J. 1986. Guide to Sampling Air, Water, Soil and Vegetation for Chemical Analysis. California Department of Food and Agriculture. Sacramento, CA. 49 pp.

(4) Office of Pesticides and Toxic Substances. September 30, 1985. Pesticide Fact Sheet (Number 68) for Diflubenzuron. United States Environmental Protection Agency. Washington, D.C. 6 pp.

(5) Dobroski, Charles J., et al. January 1985. Dimilin®: A Profile of Its Behavior in the Environment. Roy F. Weston, Inc. West Chester, PA.

(6) Bull, D.L., et al. 1978. Fate of diflubenzuron in cotton, soil, and rotational crops. J Agricul Food Chem. Volume 26(3): 515-520.

(7) Marx, R.L. 1977. Chitin synthesis inhibitors: New class of insecticides. Science. Volume 197(4309): 1170-1172.

(8) Personal communication with Juan Mercogliano. California Department of Food and Agriculture. Pest Detection and Emergency Projects. Van Nuys, CA.

(9) Neher, L.A., et al. 1982. Monitoring of the 1982 Gypsy Moth Eradication Ground Spray Program in Santa Barbara County. California Department of Food and Agriculture. Sacramento, CA. 50 pp.

(10) Franz, J.R., et al. 1985. Monitoring of the 1984 Gypsy Moth Eradication Ground Spray Program in Alameda and San Diego Counties. California Department of Food and Agriculture. Sacramento, CA. 23 pp.

APPENDIX I

Chain of Custody for Diflubenzuron

Residue Analysis

STATE OF CALIFORNIA
DEPARTMENT OF FOOD
AND AGRICULTURE

CHAIN OF CUSTODY RECORD
(use ball point pen only)

ENVIRON. MONITOR. & PEST MGMT.
ENVIRON. HAZARDS ASSESSMENT
1220 N STREET, ROOM A-149
SACRAMENTO, CA 95814

Study #	Sample #	Date On			Time On	Date Off			Time Off	Person Collecting	Location	Sample Interval	Treatment #		Sample Type
		Mo	Day	Yr		Mo	Day	Yr							
6 1				8 7				8 7							
1 2 3 4	5 6 7 8	9 10 11 12		13 14	15 16 17 18	19 20 21 22		23 24	25 26 27 28	29 30	31 32	33 34 35	36	37	38 39 40

Flow Rate	L/min	% Moisture		Units	Lab Code
41 42 43 44	45	46 47 48 49	50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75	76	77 78 79 80

Partner: Location:

Machine No.

Remarks:

Lab Results: Save extracts

For Foliage Samples MDL
Dislodgeable

Diflubenzuron

% Moisture (soil)

Chemist: Date:

KEY

Col. 1
S=Spike

Col. 2
*=split

Col. 33-35: (samp. interval)
B = background
000 = appl. day
001 = post appl. day
(etc.)

Col. 38-40: (sample type)
LOV = Lo-Vol
SOI = soil
FOL = foliage
WAT = water

Col. 77-80: (lab code)
4323 = CDFA
9527 = Cal Lab
2371 = Apple

Relinquished for Lab by: (Signature)	Date/Time	
Received by: (Signature)	Relinquished by: (signature)	Date/Time
Received by: (Signature)	Relinquished by: (Signature)	Date/Time
Received by: (Signature)	Relinquished by: (Signature)	Date/Time
Received by: (Signature)	Relinquished by: (Signature)	Date/Time
Received for Lab by: (Signature)	Date/Time	Lab #

Distribution: Original & One Copy Accompanies Shipment, copy to Coordinator Field Files.

APPENDIX II

Method of Analysis for Diflubenzuron Residue

on Leaf, and in Soil and Air Samples

CALIFORNIA DEPT. OF FOOD & AGRIC.
ENVIRONMENTAL MONITORING SECTION
CHEMISTRY LABORATORY SERVICES
3292 Meadowview Road
Sacramento, CA 95832
(916)427-4998/4999

Original Date:
Supercedes:
Current Date: 12/4/87
Method #:

Dimilin Residue in Leaf, Soil and Air Samples

SCOPE:
This method is for the analysis of Dimilin in leaf, soil and air samples.

PRINCIPLE:
Dimilin is extracted from various matrices with 50/50 hexane/acetone solution. It is then purified by passing through a normal phase small column. The analysis is by HPLC using a reverse phase column.

REAGENTS AND EQUIPMENT:

1. Hexane
2. Acetone
3. Na_2SO_4 anhydrous
4. Methylene Chloride
5. Acetonitrile
6. Methanol
7. Sep-Pak, normal phase, waters associates
8. 0.2 micron filter
9. Micro-mate syringes, 10cc.
10. Various glassware.

ANALYSIS:

1. The sample (air tube resin, leaves, or 50 grams of soil) was put in a wide mouth amber bottle with 100 ml of 50/50 hexane/acetone solution. Sonicate for 30 minutes.

2. The solvent was decanted through a bed of Na_2SO_4 into a 500 ml receiving flask.

3. Repeat steps 1 and 2 above two more times.

4. The combined solvent was evaporated to just dryness and redissolved with 5 ml of methylene chloride.

5. Using a 10 ml syringe the methylene chloride extract was passed through a normal phase sep-pak small column. Disregard the solvent.

6. Elute the sep-pak with 10 ml of acetonitrile.

7. The acetonirtile extract was evaporated to dryness and redissolved in 5 ml of methanol.

8. After passing through a 0.2 micron filter the sample is ready for the HPLC analysis.

INSTRUMENT CONDITIONS:

Perkin Elmer Series 4 HPLC with ISS-100 automatic sampler.

Column:
Dupont Zorbax Ods., 4.6 x 25mm

Detector:
Kratos spectroflow, 757

Wavelength: 254

Gradient Profile:

Time (min.)	Flow (ml/min.)	ACN	HOH
6	1.5	50	50
8	1.5	50	50
2	1.5	60	40
1	1.5	80	20

Retention Time: 9.5 minutes.

CALCULATIONS:

For air and leaves:

$$\text{ug} = (\text{std.}\ \frac{\text{ng}}{\text{ul}})\ \frac{(\text{pk. height sample})}{(\text{pk. height std.})}\ \frac{(\text{vol. std. injected})}{(\text{vol. sample injected})}\ (\text{final volume})$$

For soil:

$$\text{PPM} = (\text{std.}\ \frac{\text{ng}}{\text{ul}})\ \frac{(\text{pk. height sample})}{(\text{pk. height std.})}\ \frac{(\text{vol. std. injected})}{(\text{vol. sample injected})}\ \frac{(\text{final volume})}{(\text{sample wt.})}$$

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